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Supramolecular design of Benzene-1,3,5-Tricarboxamide with Hydrophobic Alkyl side chains toward long-range liquid crystalline properties

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Abstract. Herein we report the first approach of benzene-1,3,5-tricarboxamides (**BTAs**) with long-range liquid crystalline properties by utilizing hydrophobic alkyl side chains at the amide functional group. These compounds were successfully prepared in high yields by reacting 1,3,5-benzenetricarbonyl trichloride with series of aliphatic linear alkyl amines as the side chains. By increasing the length of hydrocarbon chains at the amino, thermograms of **BTAs** showed the formation of mesophase rangesbetween 21.8- 196.3, 41.9 - 212.4, 57.9 - 203.7, 76.1 - 207.7 and 80.5 - 200.1 degrees for decylamine, dodecylamine, tetradecylamine, hexadecylamineand octadecylamine, respectively. Such liquid crystalline properties indicate the formation of self-assembly through supramolecular interactions with a lamellar structure. In particular, benzene tricarboxamide with short alkyl chains will reduce the Van der Waals interactions to give room temperature range of mesophase structure.

1. Introduction

Supramolecular design of self-assembled organic motifs has received particular attention for the development of desired nanostructures with high performance such as liquid crystalline properties [1-3]. Many examples have been reported using πconjugated organic molecules due to the possibility to self-organize into the columnar assembly with one, two and three dimensional of nanostructures. These self-assemblies have been studied to form functional supramolecules with a control of functions at the molecular level. For practical applications, the formation of liquid-crystalline shall form disc-shape (discotic) mesophase [4, 5] not only at the room temperature but also a wide range [6-11]. For examples, Kumar and Varshney in 2000 [6] used triphenylphosphane containing branched alkyl chains at the phenyl ring to form discotic mesophase from -12 until 70 ºC.By using perylene bisimide containing alkyl chains at the both side of 3,4,5-tridodecoxybenzene, Meijer *et al*. have reported the formation of columnar mesophase at the range of -46 and 219 ºC [7]. Another approach showed triphenylene with an ethylene oxide part at the side chains of the ester functional group with a mesophase from 23 to 146.2 ºC [8]. Moreover, Sakurai *et al*. reported that fused copper porphyrin

dimer with one side of benzene-3,4-5-tridodecoxy part and another side of benzene-3,4,5-triethylene triethylene glycol part was found to form liquid crystal with a mesophase from -17 until 99 ºC [9].Metal complex can be also utilized using trinuclear gold(I) pyrazolate complexes bearing amphiphilic side chains with a mesophase range from -2.4 until 44.6 ºC [10, 11]. Recent example was to modify the core using a peptidic macrocycle with an amide functional group attached directly to the benzyl alkoxy where it formed room-temperature mesophase from -12 ºC until 77 ºC [12]. However, all of the reported liquid crystalline mesophases with such range have only achieved usingmolecular design and synthesis routes as well as expensive precursors.

Benzene-1,3,5-tricarboxamide (**BTA**) is one of the simplest πorganic motifs with only one benzene ring forπ - π stacking while the amides at the side chain can form intermolecular hydrogen bonding interactions [13]. Both interactions promote the formation of columnar assembly that is potentially developedas a building block for the preparation of supramolecular compounds with desired functions. For instant, theyhave been reported to form liquid crystalline mesophases [14, 15]. However, they are no report on the utilization of this compound for the preparation of columnar mesophase with a liquid crystalline phase in the range of room temperature. Here, we report the first **BTAs** as an organic motif for the formation of discotic liquid crystal with a room temperature range by utilizing the length of aliphatic linear alkyl amines at the side chains. In particular, commercial alkyl amines ($\mathbf{C_n\text{-}NH_2}$)as a precursor from decylamine until octadecylamine were reacted using1,3,5-benzenetricarbonyl trichloride(**BTC**) in the one-step and were simply purified to provide the above desired properties.

2. Experimental

2.1. Instrumentations

Nuclear magnetic resonance (NMR) spectroscopy for Proton (^{1}H) and carbon (^{13}C) identification wasperformed on a Bruker AVANCE 300 MHz using a deuterated chloroform ($CDCl_3$) as a solvent. The chemical shifts (δ) were internally standarized to 7.24 ppm for ^{1}H-NMR and 77.0 ppm for ^{13}C-NMR.Mass spectrometry for the determination of molecular weight wasrecorded on a AB Sciex MALDI- TOF/TOF^{TM} 5800 using an ion positive ionization and a reflection mode where the samples were crystallized using a matrix of dithranol (1,8,9-antracenetriol) in chloroform on to the top of conductive plate. Fourier Transform Infrared (FT–IR) spectroscopywas used on a model of JASCO 6800 with attenuated total reflection (ATR) as an accessory for sample measurement. Differential scanning calorimetry (DSC) thermogram was obtained using METTLER TOLEDO model DSC822^e within the temperature range of crystallization to isotropicphase with a heating and cooling rate of 10 °C min^{-1}.

*2.2. Synthesis of Alkylated Benzene-3,4,5-Tricarboxamides (**BTAs**)*

Alkylated benzene-1,3,5-tricarboxamides ($\mathbf{BTAs_{Cn}}$) were synthesized using a Schotten-Baumann amidation reaction as shown in Figure 1 [16]. Generally, it was synthesized using aliphatic primary amines ($\mathbf{Cn\text{-}NH_2}$; **C10** = decylamine, **C12** = dodecylamine, **C14** = tetradecylamine, **C16** = hexadecylamine and **C18** = octadecylamine) and **BTC**. In this reaction, a two-neck round bottom flask was used to mix$\mathbf{Cn\text{-}NH_2}$ (12.20 mmol) with **BTC** (4.08 mmol) where the mixture was stirred under vacuum for 15 minutes. This mixture was thenpurged by flowing nitrogen gas for several minutes. Dichloromethane in 80 mL was added to the mixture and then 16.30 mmol of N,N-diisopropylethylamine (DIEA, except for $\mathbf{BTA_{C10}}$using fresh destillated triethylamine) was introduced to the reaction mixture using a syringe under an inert condition. This final mixture was stirred with a magnetic bar and kept for 18 hours at room temperature. Hydrochloricacid (HCl; 0.5 M) was then used to work-up the mixture and then followed by isolation with a gravity column chromatography. This purification step used chloroform and methanol in 50 to 1 as an eluent. The collected fraction was evaporated and then dried under vaccum to give a white powder $\mathbf{BTAs_{Cn}}$ (except for $\mathbf{BTA_{C10}}$ as yellowish fibre-like solid)in the high yields. In this synthesis,$\mathbf{BTAs_{Cn}}$were synthesized in 71%, 93%, 88%, 87% and 85% yields for $\mathbf{BTA_{C10}}$, $\mathbf{BTA_{C12}}$, $\mathbf{BTA_{C14}}$, $\mathbf{BTA_{C16}}$ and $\mathbf{BTA_{C18}}$, respectively.

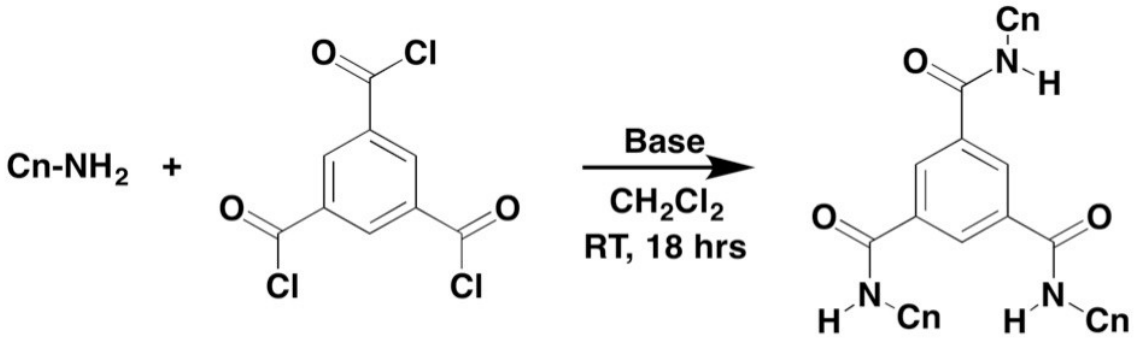

Figure 1. Synthetic scheme of $\mathbf{BTAs_{Cn}}$from primary alkyl amines ($\mathbf{Cn\text{-}NH_2}$) and **BTC** in the basic condition.$\mathbf{BTA_{C10}}$ until $\mathbf{BTA_{C18}}$ were synthesized using$\mathbf{C_{10}\text{-}NH_2}$ until $\mathbf{C_{18}\text{-}NH_2}$.

3. Results and Discussion

Figure 2 shows the mass spectra of all **BTAs** using MALDI-TOF/TOF MS spectrometer. These mass spectra gave observed molecular weight at 628.75, 712.55, 796.87, 880.73 and 964.83 Da with their molecular formulas of $C_{39}H_{69}N_3O_3$, $C_{45}H_{81}N_3O_3$, $C_{51}H_{93}N_3O_3$, $C_{57}H_{105}N_3O_3$ and $C_{63}H_{117}N_3O_3$for $\mathbf{BTA_{C10}}$, $\mathbf{BTA_{C12}}$, $\mathbf{BTA_{C14}}$, $\mathbf{BTA_{C16}}$ and $\mathbf{BTA_{C18}}$, respectively. These mass data of **BTAs** were almost similar to those of calculated **BTAs** (628.54, 712.63, 796.73, 880.82 and 964.92 Da). Moreover, the calculated monoisotopic patterns were also similar to the observed ones. These results suggested that all **BTAs** were successfully synthesized from **BTC** and $\mathbf{Cn\text{-}NH_2}$.

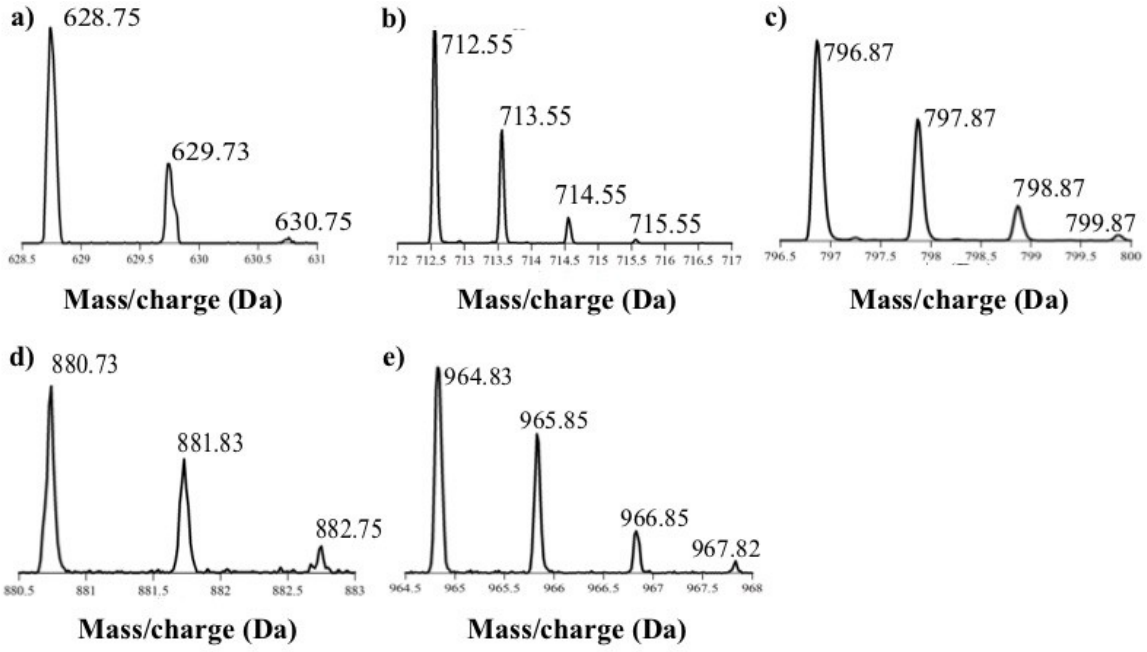

Figure 2. Mass spectra of a)BTC_{C10}, b)BTC_{C12}, c)BTC_{C14}, d)BTC_{C16} and a)BTC_{C18}.

Figure 3 shows the example of^{1}H–NMR spectra for the reactants (dodecylamine and **BTC**) and product$\mathbf{BTA_{C12}}$. The chemical shift of $\mathbf{C_{12}\text{-}NH_2}$at 2.61-2.65 ppm (triplet, 2H, $\mathbf{H_a}$ = –$NHCH_2$–) in Figure 3a was shifted to 3.47-3.40 ppm (multiplet, 6H, $\mathbf{H_a}$ = –$NHCH_2$–)in Figure 3c due to successful bonding of amino to carbonyl to form carboxamide group. Moreover, the chemical shift of **BTC**at 9.06 ppm for the benzene ring in Figure 3b was shifted to 8.35 ppm (singlet, 1H, $\mathbf{H_d}$ = Ar–H) as shown in Figure 3c, indicating attachment of alkyl amide side chains to the benzene ring. Other chemical shifts showed increasing in three times of the number of proton (Figure 3c) for the methylene

at 1.64-1.24 ppm (overlapped, 60H, $\mathbf{H_b}$ = $–CH_2–(CH_2)_{10}–CH_3$) and the methyl end group at 0.88-0.83 ppm (triplet, 9H, $\mathbf{H_c}$ = $–CH_3$). Such ^{1}H-NMR spectrum of $\mathbf{BTA_{C12}}$ was also found for that of $\mathbf{BTA_{C10}}$, $\mathbf{BTA_{C14}}$, $\mathbf{BTA_{C16}}$ And $\mathbf{BTA_{C18}}$. In particular, the integration of hydrogen from the aliphatic side chains of **BTA** provide different observed number based on its length; $\mathbf{C_{10}\text{-}NH_2}$= 48H,$\mathbf{C_{14}\text{-}NH_2}$= 72H, $\mathbf{C_{16}\text{-}NH_2}$= 84H and$\mathbf{C_{10}\text{-}NH_2}$= 96H.

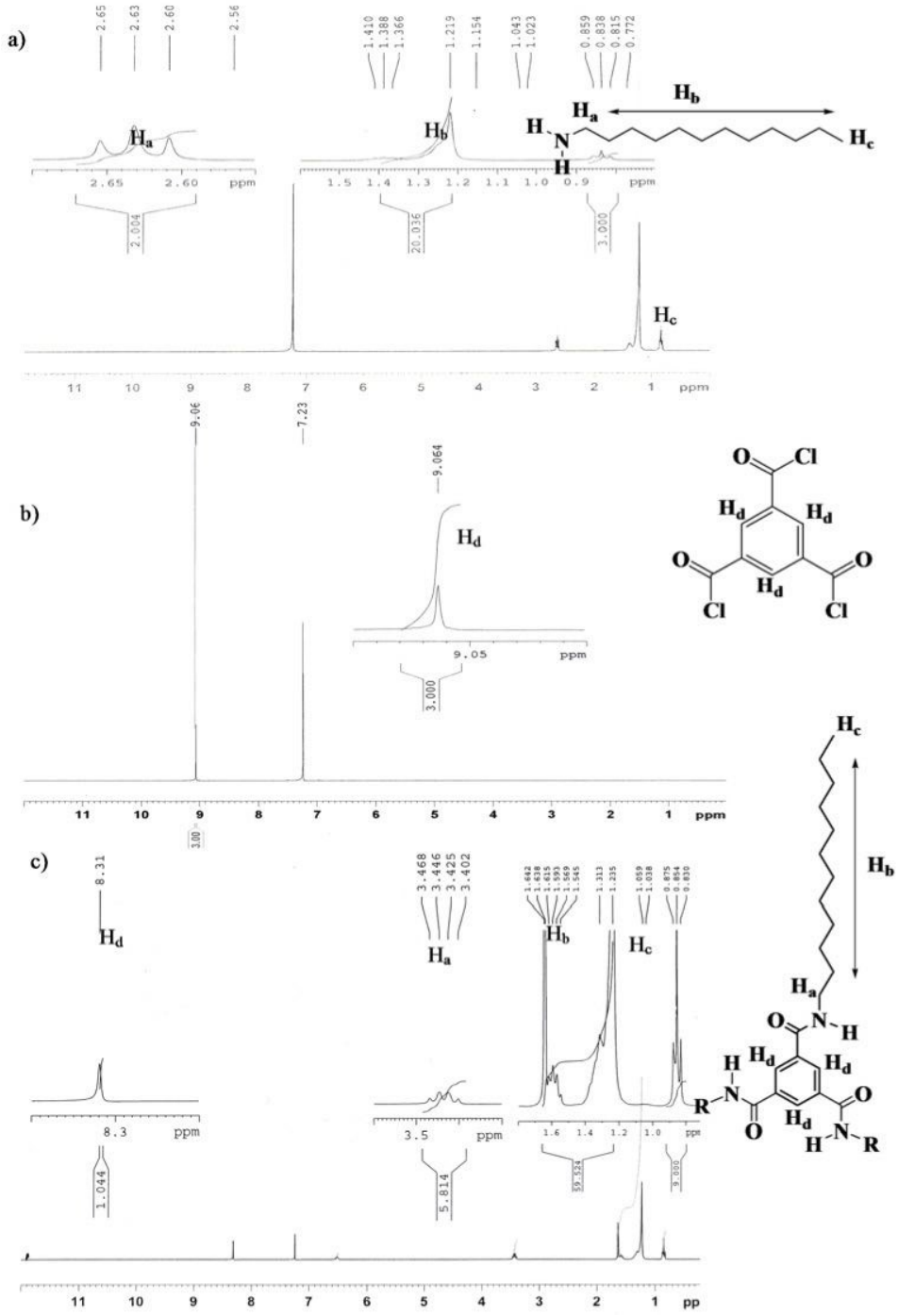

Figure 3. ^{1}H–NMR spectra for a) $\mathbf{C_{12}\text{-}NH_2}$, b) **BTC**, and c) $\mathbf{BTC_{C12}}$.

In the NMR spectroscopy, measurement with ^{13}C–NMR is also important to clarify the environment of carbon atom. Figure 4 shows^{13}C-NMR spectra of $\mathbf{BTA_{C12}}$compared to its reactant $\mathbf{C_{12}}$-

NH_2. It was found that the chemical shifts of **C_{12}-NH_2**(Figure 4a) were shifted from 41.84 to 40.19 ppm (**C_h**) while it provided the appearance of the carbonyl at 167.22 ppm (**C_i**). Such the presence of carbon at the aromatic ring was confirmed by two chemical shifts at 135.45 (**C_j**) and 127.12 (**C_k**) ppm. Other chemical shifts for the carbons gave the shifting to confirm the attachment of benzene ring to alkyl amide. Such ^{13}C-NMR spectra of **C_{12}-NH_2** were also found for that of **BTA_{C10}**, **BTA_{C14}**, **BTA_{C16}** And **BTA_{C18}** based on the number of **C_e**.

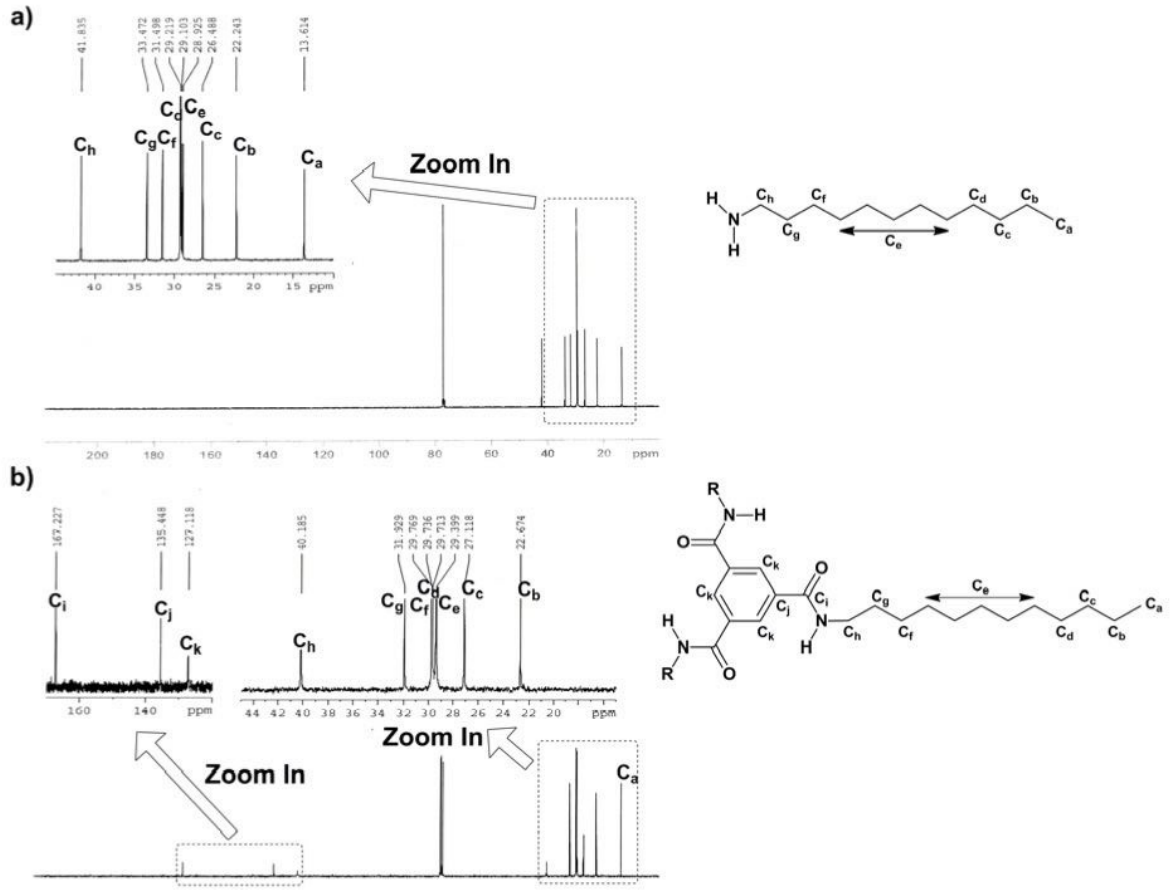

Figure 4. ^{13}C–NMR spectra for a) **C_{12}-NH_2**and c) **BTC_{C12}** using $CDCl_3$ as a solvent.

In order to support the above mass and NMR spectra, FT-IR spectroscopy measurement was performed for all **BTAs**. Figure 5 shows the FT-IR spectra of all **BTAs** in the range of 500 to 4000 cm^{-1} where diamond type of ATR was used in the sample measurement. In this measurement, N-H bonding can be observed from its stretching at 3229 and 1561 cm^{-1} for **BTA_{C10}**,3255 and 1545 cm^{-1} for **BTA_{C12}**,3231 and 1566 cm^{-1} for **BTA_{C14}**,3229 and 1561 cm^{-1} for **BTA_{C16}**and 3230 and 1562 cm^{-1} for **BTA_{C18}**. The assigned N-H stretchings for all **BTAs** have almost showed the same position of their wavenumber. Moreover, the C-H vibration was also observed for all samples where it can be assigned at 2914-2917 cm^{-1} for asymmetric stretching and 2848 cm^{-1}for symmetric stretching while the C=O stretching of amide can be observed at 1633-1638 cm^{-1}. Other vibration peaks were observed for C-C and C=C of the aromatic ring, and C-C from hydrocarbon aliphatic chains. The analysis data from mass, NMR and FT-IR spectra were confirmed the successful synthesis of all **BTAs** bearing hydrophobic side chains with C10 until C18.

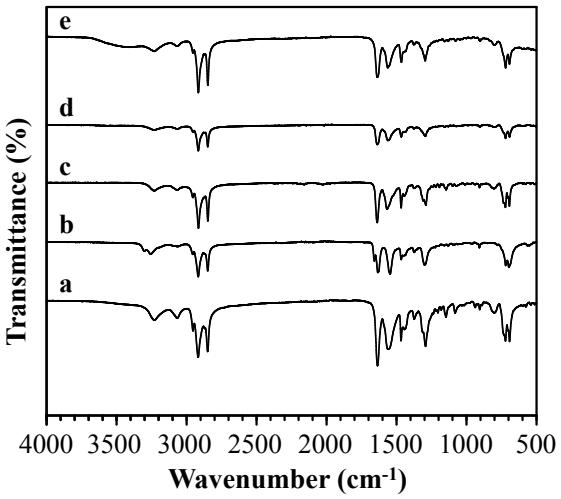

Figure 5. FT-IR spectra of a) $\mathbf{BTA_{C10}}$, b) $\mathbf{BTA_{C12}}$, c) $\mathbf{BTA_{C14}}$, d) $\mathbf{BTA_{C16}}$ and e) $\mathbf{BTA_{C18}}$.

DSC thermograms can be used to analyze the thermal behavior such as liquid crystalline (LC) properties of the synthesized **BTAs**. The thermograms of all **BTAs**was performed in the range of -10 to 210 ºC where it can record the phase transition upon heating and cooling treatment from its crystalline (**K**) to mesophase (**M**) and isotropic (**I**) phases. It was found that all **BTAs** showed the formation of mesophase in the wide range where the peaks for the formation of crystalline and columnar phases were changed with increasing in the length of alkyl chains at amide functional group. In particular, upon second heating, crystalline and columnar peaks were observed at 21.8 - 196.3, 41.9 - 212.4, 57.9 - 203.7, 76.1 - 207.7, and 80.5 - 200.1 ºC for $\mathbf{BTA_{C10}}$, $\mathbf{BTA_{C12}}$, $\mathbf{BTA_{C14}}$, $\mathbf{BTA_{C16}}$ and $\mathbf{BTA_{C18}}$,respectively. It can be seen that $\mathbf{BTAC_{10}}$as shown in Figure 6 is the only **BTAs** with mesophase range in the room temperature. Increasing in the length of alkyl chains will tend to increase the temperature for crystallization of the alkyl chain of **BTAs**. Such increasing is really possible from the requirement of higher energy to change to mesophase and isotropic phases. By modification of the length of alkyl chains at the amide functional group, such self-assembled organic motif (**BTA**) can be designed to have mesophase across room temperature in the wide range. Since many compounds with liquid crystalline properties have alkyl chains with the length at least C12 due to the flexibility and tunability, designed **BTA**will be one of the subject interests in the near future. Moreover, themesophase with long range of liquid crystalline properties can be suggested from the formation of columnar assembly of **BTA** molecules via intermolecular hydrogen bonding interaction.

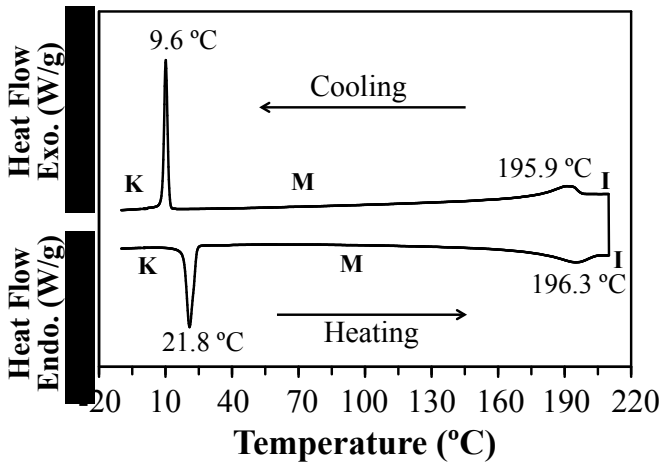

Figure 6. DSC thermogram of $\mathbf{BTA_{C10}}$ upon second heating and cooling in the range of -10 to 210 ºC (**K** = crystalline, **M** = mesophase and **I** = isotropic).

4. Conclusion

By using primary amine with different lengths from C10 to C18, the as-synthesized benzene-1,3,5-tricarboxamides bearing hydrophobic alkyl side chains at the amide functional groupwere successfully synthesized in the high yield via aSchotten-Baumann amidation reaction. The successful synthesis of **BTAs** were confirmed with NMR and FT-IR spectroscopy and mass spectrometry.These **BTAs** showed the formation of mesophase in the wide range due to the formation of columnar assembly with liquid crystalline properties from the intermolecular hydrogen bonding interaction. By increasing the lengths of alkyl chains, the crystalline peak upon heating was significantly increased from 21.8 to 41.9, 57.9, 76.1 and 80.8 ºCfor $\mathbf{BTA_{C10}}$, $\mathbf{BTA_{C12}}$, $\mathbf{BTA_{C14}}$, $\mathbf{BTA_{C16}}$ and $\mathbf{BTA_{C18}}$, respectively, while the columnar peak was only change in less than 10 ºC due to the requirement of energy in the crystallization. Indeed, the $\mathbf{BTA_{C10}}$ showed liquid crystalline properties over room temperature with such wide range in the self-assembly for the formation of columnar assembly. By using different length of alkyl chains of amine, liquid crystalline properties of **BTA** can be prepared and designed. Flexible alkyl side chains with such liquid crystalline properties in room temperature will be one of interesting subject to be explored in near future.

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References

[1] Hoeben F J M, JonkheijmP, Meijer E Wand Schenning A P H J2005*Chem. Rev.***105** 1491
[2] Kato T, Mizoshita Nand Kishimoto K2006*Angew. Chem. Int. Ed.***45** 38
[3] Bisoyi H K and Kumar S 2011*Chem. Soc. Rev.***40** 306
[4] Kumar S 2006*Chem. Soc. Rev.***35** 83
[5] Sergeyev S, Pisula W and Geerts Y H 2007 *Chem. Soc. Rev.***36** 1902
[6] Kumar S and Varshney S K 2000 *Angew. Chem. Int. Ed.***39** 3140
[7] Herrikhuyzen V J, Syamakumari A, Schenning A P H J and Meijer E W2004*J. Am. Chem. Soc*. **126**10021
[8] Kohmoto S, Mori E and Kishikawa K 2007 *J. Am. Chem. Soc*. **129** 13364
[9] Sakurai T, Shi K, Sato H, Tashiro K, Osuka A, Saeki A, Seki S, Tagawa S, Sasaki S, Masunaga H, Osaka K, Takata M and Aida T 2008 *J. Am. Chem. Soc*. **130** 13812
[10] Lintang H O, Kinbara K, Tanaka K, Yamashita T and Aida T 2010*Angew. Chem. Int. Ed.***49** 4241
[11] Azani M A, Yuliati L, Lee S L and Lintang H O 2018 *Malay. J. Fund. Appl. Sci*. Special Issue on Chromatography and Other Analytical Techniques 133
[12] Sato K, Itoh Y and Aida T 2011 *J. Am. Chem. Soc*. ***133*** 13767
[13] Cantekin S, de Greef F A and Palmans A R A 2012*Chem. Soc. Rev*. **41** 6125
[14] Stals P J M, Haveman J F, Martin-Rupun R, Palmans A R A and Meijer E W2009*J. Chem*.*Chem*.**19**124
[15] Fitie C F C, Roelofs W S C, Kemerink M and Sijbesma R P 2010 *J. Am. Chem. Soc*. ***132*** 6892
[16] Matmin J, Yuliati L, Shamsuddin M and Lintang H O 2014 *Adv. Mater. Res.* **925** 228